PEROVSKITE MANGANITES: A NEW FAMILY OF MATERTIALS FOR UNCOOLED/ MODERATELY COOLED IR DETECTOR APPLICATIONS

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ABSTRACT

Alkaline earth doped perovskite manganites have been a focus of research during the past several years on account of the phenomenon of colossal magneto-resistance (CMR) and its application in magnetic information storage technology. Somewhat less known is the potential of these materials for use as bolometric infrared detectors. The bolometric sensor functionality is based on the steep temperature dependence of resistance in the vicinity of the insulator-metal transition. The insulator-metal transition temperature can be tuned by manipulating the chemistry, which makes it feasible to tailor these materials for sensor operation over a wide temperature range anywhere from well over room temperature down to liquid nitrogen and lower temperatures. Figure of merit calculations based on the best currently demonstrated values of the temperature-coefficient of resistance and 1/f noise indicate good potential for development of state-of-the-art IR detectors based on manganites.

INTRODUCTION

Perovskite rare earth manganites, also popularly known as "colossal magnetoresistive (CMR) oxides, have recently been a focus of materials research [1,2]. From the applications perspective, interest in these materials arose initially from their unusually large magnetoresistance. However, recently it has been realized that CMR manganites have promising potential for bolometric infrared detection in a wide range of temperatures from room temperature down to liquid nitrogen temperatures [3,4]. The operating temperatures can be tuned over a wide range by simple variations in chemistry.

The bolometric application of CMR manganites is based on the steep drop in resistivity with temperature accompanying an insulator-metal transition . The CMR Manganites are derived from rare earth manganese oxides such as (La, Nd or Pr) MnO_3 which are antiferromagnetic insulators. The insulator-metal transition is brought about by the partial substitution of the trivalent rare earth site by divalent alkaline earth elements, thereby driving manganese ions into a mixture of two valence states, Mn (3+) and Mn (4+). The electron transport between these two types of Mn ions is coupled to the alignment of the core Mn spins via Hund's coupling. To put it very simply, based on the concentration of Mn (4+) ions (determined by the amount of alkaline earth substitution) along with several structural factors (partly related to the average ionic radius of the rare earth site), ferromagnetic ordering accompanied by metallic electron transport becomes energetically favorable over the antiferromagnetic insulating state below a certain temperature. This results in the insulator-metal (I-M) transition which is the phenomenon relevant to the bolometric application. The temperature at which slope of the resistance vs temperature is steepest (i.e. the optimal operating point of the bolometer) occurs typically about 10 –15 K below the I-M transition. Fig.1 shows the insulator-metal transition and the associated bolometric optical response of a

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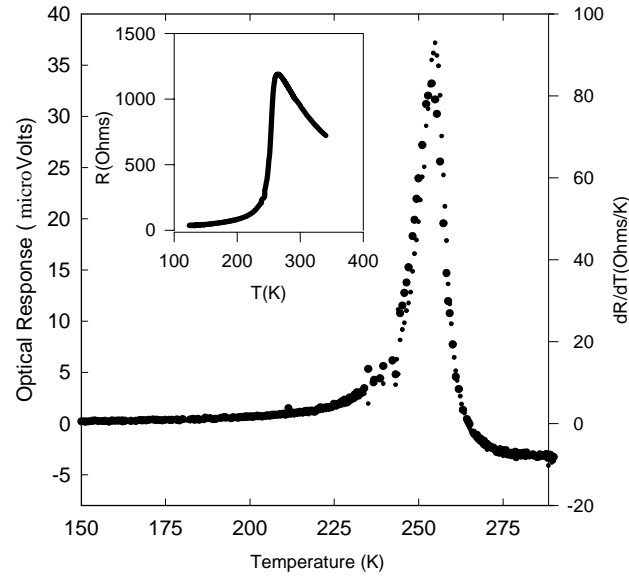[1] *Contact information for M.R. Rajeswari - Email: mrajewari@towson.edu*

Fig.1 : *Bolometric optical response and dR/dT of a $La_{0.67}Ca_{0.33}MnO_3$ thin film. Inset shows the insulator-metal transition (Ref. 3) .*

of a manganite thin film [3] .The I-M transition temperature in turn depends on the choice of the rare earth and alkaline earth elements and the amount of alkaline earth substitution. The material composition can therefore be tailored for the desired operating point of the bolometer depending on the application. The range of such tunability is quite broad, spanning a temperatures range from several tens of degrees above room temperature down to liquid nitrogen temperatures, including uncooled operation at room temperature.

Table-1: *A partial list of manganite materials for uncooled/moderately cooled bolometer application.*

Materials Composition	Peak Temperature (K)	TCR (%/K)	Peak Resistivity ($m\Omega$-cm)
$La_{0.7}Ba_{0.3}MnO_3$	330	4	17.5
$La_{0.7}Sr_{0.3}MnO_3$	380	2.5	0.5
Ag-doped $La_{0.7}Ca_{0.3}MnO_3$	285	18	8.0
$Nd_{0.7}Sr_{0.3}MnO_3$	235	32	40.0
$Pr_{0.7}Sr_{0.3}MnO_3$	320	11	8.0
$La_{0.9}Sr_{0.1}MnO_3$	277	5	14.0
$La_{0.37}Pr_{0.30}Ca_{0.33}MnO_3$	230	58	200
$La_{0.8}Ca_{0.2}MnO_3$	298	8	12.0
$Nd_{0.6}Sr_{0.4}MnO_3$	215	7	60.5

RELEVANT MATERIAL PROPERTIES

Several CMR material compositions have been investigated and shown to be potential candidates for bolometric application. The data presented here are on epitaxial thin films grown by the Pulsed Laser Deposition (PLD) technique which has been established as the technique of choice for the growth of the best quality manganite films. The following is a summary of the current status of materials properties that are relevant to the IR detector application.

Temperature Coefficient of Resistance (TCR)

One of the key figures of merit for the bolometric application is the temperature-coefficient of resistance (TCR, defined as $1/R \, dR/dT$). Several CMR materials have been shown to have insulator-metal transitions and remarkably high values of TCR in the temperature range 200 K – 300 K(see table-1). TCR values as high as 8 % at room temperature which is significantly higher compared to < 3%/K of Vanadium Oxide and 3-4%/K for semiconducting YBCO. CMR manganites hold even better promise for applications that are compatible with lower temperatures of operation. TCR as high as 18%/K has been demonstrated at 270 K and 58%/K at 200 K. The manganite family also offers the potential for development of detectors for operation at lower temperatures below 100 K by tuning the chemistry to achieve lower insulator-metal transition temperatures . Comparison of different manganite materials indicates that TCR increases as the insulator-metal transition temperature shifts to lower temperatures [5]. Highest values of TCR are observed in materials which show percolative insulator-metal transitions accompanying phase separation (e.g. $La_{0.37}Pr_{0.33}Ca_{0.33}MnO_3$ in table-1). However, percolative transitions are characterized by thermal hysteresis and larger noise values which are not desirable for bolometric applications. (Note that except for $La_{0.37}Pr_{0.33}Ca_{0.33}MnO_3$, none of other materials listed in table-1 show thermal hysteresis, which is another advantage over vanadium oxide which exhibits hysteresis at room temperature).

Electrical Noise

Another key materials property of interest from the perspective of bolometric applications is the electrical noise, which includes Johnson noise, and 1/f resistance noise. Since the resistivity of these materials is rather low , Johnson noise is not expected to be a concern. A major concern in the initial phase of our research was the anomalously large magnitudes of 1/f noise, which these materials were shown to exhibit [5,6]. However, continued efforts at improving the materials quality have resulted in significant reduction of 1/f-noise magnitudes by several orders of magnitudes [7]. Fig.2 shows the normalized noise power spectral density κ evaluated according to the Hooge model as

$$\kappa = S_v f^{1/2} \, v \, / V_{dc}^2$$

where S_v is the noise power spectral density, f is the frequency, v is the sample volume and V_{dc} is the dc voltage.
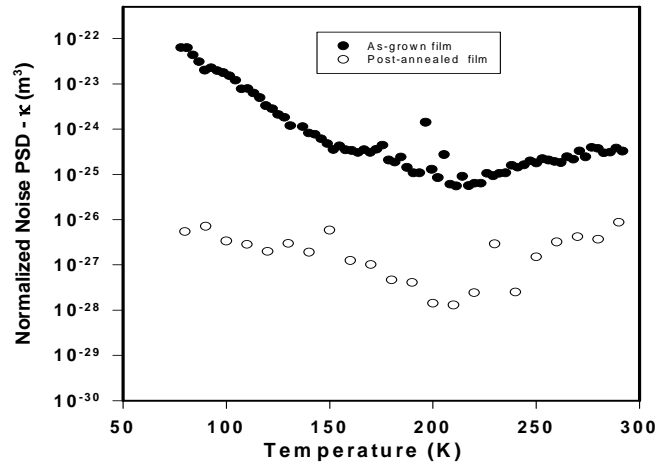

Fig.2 : *Normalized noise power spectral density of an as-grown and post-annealed La $_{0.67}Ca_{0.33}MnO_3$ film as a function of temperature (Ref.7).*

Oxygen stoichiometry has been identified to be a key parameter that influences the noise magnitudes and novel materials modification schemes to promote enhanced oxygenation have been developed. One such scheme involves the addition of a small amount of Ag [8] (5-10 weight %) which has been shown to increase the I-M transition temperature via enhanced oxidation. Recently it has been demonstrated that noise values at room temperature are only marginally higher than that of Vanadium Oxide [9]. Thus 1/f noise is no longer considered to be an insurmountable hurdle for the bolometric application of manganite thin films.

Growth of epitaxial manganite thin films on Si

In addition to possessing the materials properties relevant to the figures of merit for the bolometric application, it is also necessary that the candidate material be compatible with growth of high quality thin films on substrates such as Si for the fabrication and demonstration of actual bolometric detectors. Si is a preferred substrate for thermal IR detectors on account of its thermal properties (low heat capacity and high thermal conductivity), micro-machinability (facilitating detector fabrication on micro-machined membranes in air-bridge structure, thus reducing the device thermal mass and providing enhance thermal isolation) as well as the potential for integration of the detector with measurement or read-out electronics on a single chip. However, Si is chemically reactive with the manganites at high temperatures and also has the disadvantage of large thermal expansion coefficient mismatch (as in the case of YBCO). This calls for lattice-engineering schemes employing buffer and template layer growth for the integration of CMR Manganite films with Si. Yttria stabilized Zirconia (YSZ) is used as the buffer layer to avoid the chemical reaction with the Si substrate. YSZ however has a large lattice mismatch with the manganites which necessitates the growth of a lattice-matched template layer over the YSZ layer to ensure good crystallinity of the manganite film. $Bi_3Ti_4O_{12}$ (BTO) has been shown to be an effective template layer facilitating the growth of high quality manganite films on Si [10,11].
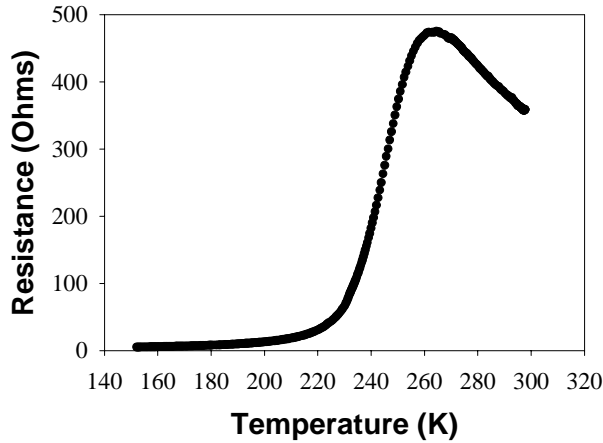

Fig.3 : *Metal-insulator transition in a Pr $_{0.67}$ Sr $_{0.33}$ MnO$_3$ thin film grown on Si.*

TCR and noise values of manganite thin films grown on Si employing the above mentioned schemes are comparable to the best-demonstrated values on other substrates. A typical result showing the resistivity and TCR of La $_{0.7}$ Pb $_{0.3}$ MnO$_3$ thin film on Si is shown in Fig.3.

Figure of merit calculations

We have calculated the achievable figure of merits for manganite bolometers based on the best demonstrated values of TCR and noise in epitaxial thin films. Table 2 shows the results of our calculations of the noise equivalent power (NEP) and detectivity D*. The calculations are for a device patterned into a meander line on 1 μm micro-macined Si membrane with state-of-the-art thermal isolation of the transducer element. We assume device area = 1 mm2, bias Current = 1 μA , operating Frequency = 30 Hz, thermal conductance G= 6*10 $^{-8}$ W/K and heat capacity C=7*10 $^{-10}$ J/K. Note that the only noise sources

considered are Johnson noise and 1/f noise of the sensor material. We have not take into account noise sources from the electronics in these estimates which therefore do not represent practically achievable values. In other words, the figures-of-merit in table-2 serve mainly to indicate the limitations based on material properties alone. The projected NEP and D* values of the manganite detectors compare well with those of the state-of-the-art bolometric detectors operating close to room temperature.

Table-2: *Figure of merit calculations based on best TCR and noise values currently demonstrated*

Operating Temperature	Material	TCR or β (dlnR/dT)	Device Resistance (Ohms)	Responsivity (V/W)	NEP W/ √Hz	Effective Detectivity D*(cm √Hz/W)
295 K	Pb-doped $LaCaMnO_3$	.07	60,000	3.2×10^3	9.9×10^{-12}	2.6×10^9
270 K	Ag-doped $LaCaMnO_3$	0.18	60,000	8.2×10^3	3.7×10^{-12}	7×10^9
220 K	$NdSrMnO_3$	0.4	300,000	9.1×10^4	6.8×10^{-13}	3.8×10^{10}
240 K	$LaCaMnO_3$	0.22	60,000	1×10^4	2.9×10^{-12}	8.9×10^9

SUMMARY

The results presented above clearly show that the family of CMR manganites offer several candidate materials for the development of bolometric IR detectors in the temperature range from room temperature to below 200 K. The temperature range can be extended to lower temperatures below a 100K by tuning the chemical composition. The temperature coefficient of resistance close to room temperature is superior to that of materials like vanadium oxide and semiconducting YBCO which are currently being actively pursued for uncooled IR detector applications.   High quality manganite films have been demonstrated on Si employing buffer and template layer growth schemes. The figure of merit calculations based on the best values of TCR and 1/f noise currently achieved indicate the potential for achieving manganite based detectors with state-of-the-art performance. Manganites are stable and robust materials. An added advantage offered by the manganites is the feasibility of developing a generic materials technology for IR detectors for a wide operating temperature range thus catering to a wide spectrum of users.

REFERENCES

1. S. Jin et al, Science <u>264</u> 413 (1994).
2. T. Venkatesan et al, Phil. Trans. Roy. Soc. London <u>A356</u> p1661 (1998).
3. M. Rajeswari et al, Appl. Phys. Lett. <u>68</u> 3555 (1996).
4. A. Goyal et al, Appl. Phys.Lett. <u>71</u> 2535 (1997).
5. M. Rajeswari et al, Appl. Phys. Lett. <u>69</u> 851(1996).
6. G.B. Alers et al Appl. Phys. Lett. <u>68</u> 3644 (1996).
7. M. Rajeswari et al, Appl. Phys. Lett. <u>73</u> 2672(1998).
8. R. Shreekala et al, Appl. Phys. Lett. <u>74</u> 2857(1999).
9. I. Gergis, Rockwell Science Center (Private Communication).
10. Z .Trajanovic et al, Appl. Phys. Lett. <u>69</u> 1005(1996).
11. M. Rajeswari et al (to be published)